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12

# PATENT APPLICATION

A1

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54 Hollow fibers, process for manufacturing them and their applications, particularly in the area of membrane separations.

57 The invention relates to hollow fibers on the basis of fibrogenic polymer substances characterized by the fact that they have an asymmetrical structure, in that they have a relatively dense layer ("skin") H of very small thickness < 1 µm on their outer periphery, which is connected with a structure called "open" J of which the porosity increases as the internal wall is approached, said open structure subjacent to the said skin making up a microporous structure directly in contact with the said skin and characterized by the presence of pores with dimensions greater than 0.1 µm and less than 2µm and with a macroporous layer having macrovoids I having a main dimension greater than 2 µm, the ratio of these macrovoids representing at least 10% of the wall volume.

[drawing]

[illegible] NATIONAL PRINTING OFFICE. 27 Rue de la [illegible] – 75732 PARIS CEDEX 15

[in left margin] **FR 2 566 003 – A1**

The present invention relates to hollow fibers on the basis of fibrogenic polymer substances.

A certain number of hollow fibers on the basis of fibrogenic polymer substances having asymmetrical structures is already known. Such asymmetrical structures generally belong to one of the following classes:

– the class of structures having a relatively dense layer, hereinafter called "skin," on the periphery of the internal channel of the fiber with, as a notable characteristics, an increasing porosity (from the interior to the exterior of the fiber) and the presence of macrovoids between this internal skin and the external periphery of the fiber. A fiber such as this is illustrated in figure 1 (cross section view along a plane perpendicular to the longitudinal axis of the fiber) of the drawings attached. With reference to this figure, a portion of the internal skin is indicated with A, the macrovoids with B, reference C indicating the external periphery of the fiber and arrow F symbolizing increasing porosity from the interior to the exterior of the fiber. The fibers having such a structure are e.g., those disclosed in U.S. patents No. 3.526.388, 3.615.024, 3.423.491;

– the class of structures having, as in the preceding case, an internal skin and a porosity increasing from the interior toward the exterior of the fiber but the absence of macrovoids. Figure 2 thus illustrates a fiber of this class, A indicating the internal skin, D the section between this internal skin and the periphery C, in which the absence of macrovoids can be seen and the arrow F symbolizing the porosity increasing from the interior toward the exterior of the fiber. Such fibers are disclosed, e.g., in U.S. patent no. 4.051.300;

– the class of structures having an internal skin and an external skin, these two skins located on either side of a section of the fibers having a majority of the macrovoids. A fiber such as this is illustrated in figure 3 of the attached drawings. In this figure, A indicates the internal skin, E the external skin and between the two, the macrovoids B. The porosity of this type of fibers is also increasing, but in the direction of the two arrows $F_1$ and $F_2$. This type of fiber is disclosed, e.g., in French patent 77.34031;

– the class of structures not having, in contrast to the classes described above, an internal skin but in contrast having only an external skin. Such fibers do not have macrovoids between the exterior and the interior of the fiber. Their porosity increases from the exterior toward the interior. Figure 4 illustrates such a fiber. The external skin is indicated by E and the porous layer by D, the porosity in this case increasing in the direction of arrow $F_3$. Such fibers are disclosed, e.g., in French patent 30.06858;

– the class of structures having, as in the case of the fibers illustrated in figure 3, an internal skin and an external skin, but with the presence of macrovoids between these two skins. A fiber such as this is illustrated in figure 5. A and E designate, respectively, the internal and external skins with a certain proportion of macrovoids and of microvoids (B and D). In this case, the porosity increases in the direction of the two arrow $F_4$ and $F_5$. Such fibers are disclosed, e.g., in French patent 79.11031;

– and finally, the class of structures not having any skin, as illustrated in figure 6, a figure in which the porous structure between the internal periphery G and the external periphery C simultaneously has macrovoids and microvoids, D and B, respectively. This type of fiber is disclosed, e.g., in French patent 73.15427.

In contrast, the present invention produces hollow fibers with asymmetrical structure differing from the various structures mentioned above, in that they have a relatively dense layer ("skin") of very small thickness (< 10,000 Å) on their external periphery, which is connected to a structure in which the porosity increases toward the internal face.

According to other characteristics:

– the structure subjacent to the said skin is a structure called "open" advantageously made up of a microporous layer directly in contact with the said dense skin and characterized by the presence of pores with sizes greater than 1,000 Å and less than 2 μm and a macroporous layer having macrovoids with a main dimension greater than 2 μm, the proportions of these macrovoids representing at least 10% of the volume of this structure;

– the said macrovoids with dimensions greater than 2 μm are advantageously oriented radially and they may be open on the side of the internal face of the fiber although they are not on the side of the skin;

– the said external skin is also characterized by the essential absence of pores with diameter greater than 1,000 Å;

– the macrovoids of the macroporous structure have the shape of fingers, advantageously of cylindrical form with variable length which can reach more than 9/10 of the thickness of the fiber wall;

– the diameter of the circular section of the macrovoids is generally greater than 5 μm.

The hollow fibers according to the invention are on the basis of any fibrogenic polymer that can be dissolved in a solvent and coagulated in a non-solvent.

Among the examples of polymers that are able to form the fibers according to the invention, it is possible to mention vinylidene polyfluorides, polysulfones, polyacrylonitriles, cellulose and cellulose esters, vinyl polychlorides, vinyl polyacetates, polyamides, polyimides, polycarbonates, phenylene polyoxides, polystyrenes and more generally, polyethers, polyesters, aryline polyoxides, polysulfides, polyvinyl polymers, polyallylic polymers, polyazones and polyimidazoles, polyphosphazines, polyhydrazides or this fibrogenic polymer may even be chosen from among the copolymers or mixtures of polymers made up using at least one of the polymers above.

The fibers in question may be obtained by using any known technique and, in particular, the extrusion technique called "dry-humid method."

According to this technique, a solution of the polymer in its solvent is extruded in an extrusion die, advantageously of an annular type, with an injection of a gas, of a vapor or a liquid through the hole of the extrudate, then passing the hollow fiber obtained in a coagulation bath.

In order to obtain the hollow fibers in the invention such as defined above using this technique, the following is planned:

– to add at least one specific additive to the polymer solution in its solvent;

– to inject a specific fluid through the hole of the extrudate.

The specific additive is chosen from among the molecules that make it possible to obtain a solution that is macroscopically homogeneous with the solvent-polymer pair, while being able to be extracted from the fiber at the time of coagulation of the latter or by using any appropriate post-treatment. The following can be mentioned as examples of additive molecules corresponding to the definition above: macromolecules with molar mass greater than 500 of either the polyvinylpyrrolidone type, polyvinylpyridine, polyvinylic alcohol, polyethylene glycol, polyacryl amides, polyacrylic acids, either ionic or nonionic surfactant agents containing in their molecule simultaneously at least one hydrophobic unit and at least one hydrophilic unit (ionic or nonionic), it being possible for the hydrophobic unit to be of the polyoxyethylene type.

The specific internal injection fluid may be a liquid or a gas and it contains an adequate quantity of at least one solvent of the fibrogenic polymer to prevent the said fluid from rapidly coagulating the solution containing the fibrogenic polymer.

The scope and the inventive nature the invention will be seen more clearly in the description to follow, with reference to the drawings attached, in which:

– figures 1 to 6, which have already been described, illustrate different types of known fibers;

– figure 7 is a schematic diagram established on the same basis as figures 1 to 6, illustrating the cross section of a fiber according to the invention;

– figures 8, 9 and 10, 11 are different photographic views taken with an electron microscope of a fiber according to the invention and,

– figure 12 is diagram explaining the process used to create a fiber according to the invention.

With reference to these figures, especially the photographic enlargements 8 and 9 (axial cross section), they an external skin designated by H in the diagram in figure 7; a porous structure having macrovoids I in the form of elongated fingers open toward the interior, as can be seen more precisely in the photographic enlargement 10. In fact, this photographic enlargement corresponds to a shot

taken inside the fiber. The essentially circular craters that can be distinguished there correspond to the end of these fingers. On this enlargement, microvoids J can also be distinguished. As far as the external skin H is concerned, it appears in the photographic enlargement 11 which shows the density of this skin without clearly visible voids. Taking into account this structure, it is clear that the porosity of the fiber increases from the exterior toward the interior.

For greater precision, it should be noted that in the photographic enlargement 8, 1 cm = 50 μm; in enlargement 9, 1.5 cm = 25 μm; in enlargement 10, 1 cm = 5 μm; and in enlargement 11, 1 cm = 1 μm.

In order to obtain the hollow fibers thus illustrated, preferably the extrusion technique called "dry-humid method" is used. This technique is shown schematically in figure 12.

A reservoir 1 of polymer solution, advantageously equipped with a filter 3a, allows this solution into the die 6, shown in larger scale, under pressure, due to the introduction of an inert gas, e.g., nitrogen, supplied from the gas bottle 2, this pressure being controlled by gauge 3. The polymer solution coming from reservoir 1 includes a solvent for this polymer and at least one additive as described above, i.e., either a macromolecule with molar weight greater than 500 or an ionic or nonionic surfactant (hydrophilic-hydrophobic).

At the same time, the fluid containing the solvent as described above is allowed into the annular orifice of this die 6. Naturally, the fluid coming from reservoir 4 and its admission into the die is carried out by means of a flow meter 5 that controls the feed and a valve 8 that is controlled as a function of the desired flow. A motor 9, for winding the fiber 10, downstream of the coagulation vat 7 containing the coagulating solution simultaneously allows for control of the drawing tension of the fiber and its storage.

The coagulating solution can be chosen from among any appropriate non-solvents. Preferably this will be water.

By proceeding in this way, the asymmetry of the hollow fiber according to the invention is obtained due to different coagulation of the two faces of the extrudate. The external face of the fiber coagulates quickly in contact with the non-solvent of the polymer, while a very slow coagulation is

produced on the interior face since it is in contact with the solvent contained in the fluid injected into the central part of the annular orifice of die 6.

In an advantageous manner, this type of extrusion is carried out by using extrudable solutions that are able to form a solid precursor having viscosities of around 5 pascal-second to 1,000 pascal-second or more at the extruding temperature.

In addition, the non-solvent and the solvent may be miscible and preferably in all proportions and the additive may advantageously be eliminated from the fiber by simple washing using a solvent of same, but naturally not a solvent of the polymer.

It is obvious that the stronger the non-solvent of the polymer, the greater the asymmetry and the less the total coagulation time before washing and storage.

In the following examples, characterization of the porosity is carried out by observing the photograph obtained by electron scanning microscopy. If this technique makes it possible to insure that the skin does not have pores with a dimension greater than 1,000 Å (0.1 μm), it does not make it possible to detect easily and with certainty the pores of smaller dimension. Water permeability has been used to verify the presence of finer pores. A procedure to measure water permeability consists of forming a loop of several hollow fibers. The open end of the hollow fibers is enclosed in a sheet of tubes. This loop is then placed in a cylindrical envelope. The water under pressure is introduced into the envelope and the water that has crossed the wall of fibers by way of the open end of the loop is collected.

The relationship between the quantity of water collected (expressed in $m^3$ per second and by $m^2$ of the surface) and the difference in pressure applied on either side of the wall of the fiber (expressed in pascals) is used to indicate the hydraulic permeability. It has the unit $m^3/m^2 \cdot s$ Pa or m/s · Pa. All the permeabilities are measured at the temperature 25°C.

Example 1

Starting with a solution made up of polysulfone ("Udel 3500") with 29% "Triton X 100" at 22% and N-N-dimethylformamide at 49% (% by mass), extrusion of a hollow fiber was carried out with the

method described and with N-N-dimethylformamide as internal injection fluid and water as a coagulant.

Its external diameter is 580 μm and its internal diameter is 440 μm.

The hollow fiber has the structure according to the invention:

– on its external face, a "skin" is found that does not contain pores with diameter greater than 1,000 Å;

– the open structure subjacent to the external skin is made up of a microporous layer with thickness 30 μm having pores whose largest size is around 1.5 μm, and a macroporous layer presenting macrovoids with cylindrical shape oriented radially that open out to the internal face having a length of around 40 μm and a diameter on the internal face around 14 μm. These macrovoids occupy around 20% of the volume of the wall.

The presence of pores with diameter less than 1,000 Å in the skin is proven by the water permeability:

$Lp_{25°C} = 6.9 \cdot 10^{-10}\ m^3/m^2 \cdot s \cdot Pa$

Example 2

A hollow fiber was extruded using a solution made up of vinylidene polyfluoride ("PCUK 1000") at 28%, "Triton X100" at 18% and N-N-dimethylformamide at 54% (% by weight), with N-N-dimethyl acetamide as internal injection fluid and water as the coagulant. Its external diameter is 580 μm and its internal diameter is 440 μm.

The hollow fiber presents the structure according to the invention:

– on its external face there is a skin containing pores with a diameter no greater than 1,000 Å;

– the open structure subjacent to the external skin is made up of a microporous layer with thickness 4 μm having pores of which the largest has a size around 0.5 μm and a macroporous layer having macrovoids with cylindrical shape oriented radially, and opening out into the internal face, having around 121 μm length and 15 μm diameter on the internal face. The macrovoids occupy around 40% of the volume of the wall.

The presence of pores with diameter less than 1,000 Å in the external skin is proven by the water permeability:

$Lp_{25°C} = 2.6 \cdot 10^{-10}\ m^3/m^2 \cdot s \cdot Pa$

Example 3

A hollow fiber was extruded using a solution made up of polysulfone ("Udel 35000") at 18%, polyvinylpyrrolidine "K15" at 18% and N-N-dimethylformamide at 64% (% by weight), with N-N-dimethylformamide as internal injection fluid and water as the coagulant. Its external diameter is 430 μm and its internal diameter is 150 μm.

The hollow fiber presents the structure according to the invention:

– on its external face there is a skin containing pores with a diameter no greater than 1,000 Å;

– the open structure subjacent to the external skin is made up of a microporous layer with thickness 20 μm having pores of which the largest has a size around 1 μm and a macroporous layer having macrovoids with cylindrical shape oriented radially and opening out into the internal face having around 120 μm length and 10 μm diameter on the internal face. The macrovoids occupy around 60% of the volume of the wall.

The presence of pores with diameter less than 1,000 Å in the external skin is proven by the water permeability:

$Lp_{25°C} = 0.4 \cdot 10^{-10}\ m^3/m^2 \cdot s \cdot Pa$

Example 4

Extrusion without addition of additive.

A solution of 29% polysulfone ("Udel 3500") and 71% N-N-dimethylformamide is prepared.

This solution is extruded using the procedure described using N-N-dimethylformamide as the internal injection fluid. Upon examination of the fiber obtained, it is confirmed that it contains an external skin and a subjacent open structure with the presence of macrovoids, of which some open out to the internal face. However one of the characteristics of this fiber extruded without additive is that its permeability to water is very weak, which thus demonstrates that the skin has very few pores:

$Lp_{25°C} < 10^{-12}\ m/s \cdot Pa$

Example 5

Extrusion in the presence of water in the internal injection fluid.

A solution is produced identical to the one in Example 1. This solution is extruded according to the procedure described using a fluid of the following type as the internal injection fluid:

– N-N-dimethylformamide 90% }
} % by mass
– Water 10% }

A hollow fiber is obtained. Its external diameter is 350 μm and its internal diameter is 110 μm.

The hollow fiber presents the structure according to the invention:

– on its external face there is a skin containing no pores with a diameter greater than 1,000 Å;

– the open structure subjacent to the external skin is made up of a microporous layer with thickness 7 μm having pores of which the largest has a size around 1.5 μm and a macroporous layer having macrovoids with cylindrical shape oriented radially and opening out into the internal face having around 107 μm length. The macrovoids occupy around 40% of the volume of the wall.

One of the characteristics of the fiber extruded with the presence of 10% water in the internal injection fluid is that the macrovoids which are around 16 μm in diameter in the wall become narrower such that they have a surface no greater than 2 μm when they open out into the internal face.

The presence of pores with diameter less than 1,000 Å in the external skin is proven by the water permeability:

$Lp_{25°C} = 0.46 \cdot 10^{-10}\ m^3/m^2 \cdot s \cdot Pa$

The hollow fibers obtained according to the invention have interesting applications in various areas and in particular, they can be used directly in ultrafiltration or in microfiltration, in the area of dialysis, in the area of reverse osmosis, in the area of gaseous or pervaporation, or even as a liquid membrane support.

Naturally the present invention is only described by way of an example and in a non-limiting manner and any useful modification could be applied to it without leaving the scope of the invention.

## CLAIMS

1. Hollow fibers on the basis of fibrogenic polymers characterized by the fact that they have an asymmetrical structure in the sense that they have a relatively dense layer ("skin") (H) of very small thickness (< 1 μm) on their external periphery, which is connected to a structure called "open" (J) of which the porosity increases when directed toward the internal face, the said open structure subjacent to the said skin making up a microporous layer directly in contact with the said skin and characterized by the presence of pores with dimensions greater than 0.1 μm and less than 2 μm and a macroporous layer having macrovoids (I) with a main dimension greater than 2 μm, the proportion of these macrovoids representing at least 10% by volume of the wall.

2. Hollow fibers according to claim 1, characterized in that the said macrovoids of size greater than 2 μm are advantageously oriented radially and they may be open on the side of the internal face of the fiber while they are not on the side of the skin.

3. Hollow fibers according to either one of claims 1 or 2, characterized in that the said external skin is permeable to water and also characterized by the essential absence of pores with diameter greater than 1,000 Å.

4. Hollow fibers according to any one of claims 1 to 3, characterized in that the macrovoids of the structure subjacent to the skin have the form of fingers arranged radially, advantageously with a shape that is essentially cylindrical with variable length that may reach up to more than 9/10 of the thickness of the total wall of the fiber.

5. Hollow fibers according to claim 4, characterized in that the diameter of the circular section of the macrovoids is generally greater than 5 μm.

6. Hollow fibers according to any one of claims 1 to 5, characterized in that they are based on any fibrogenic polymers that can be dissolved in a solvent and coagulated in a non-solvent.

7. Hollow fibers according to claim 6, characterized in that the fibrogenic polymer is chosen from among vinylidene polyfluorides, polysulfones, polyacrylonitrile, cellulose and cellulose esters, vinyl polychlorides, vinyl polyacetates, polyamides, polyimides, polycarbonates, phenylene polyoxides, polystyrenes and more generally, polyethers, polyesters, aryline polyoxides, polysulfides, polyvinyl polymers, polyallylic polymers, polyazones and polyimidazoles, polyphosphazines, polyhydrazides; or this fibrogenic polymer may even be chosen from among the copolymers or polymer mixtures made up of at least one of the polymers above.

8. Procedure for fabrication of hollow fibers according to any one of claims 1 to 7, characterized in that the fibrogenic polymer is dissolved in a solvent at a concentration appropriate for extrusion, at least one additive is added, chosen from among either macromolecules with molar weight greater than 500 or from among ionic or nonionic surfactants; the solution containing the polymer, the solvent and the additive is passed through an extrusion die, advantageously of the annular type, simultaneously a fluid is injected through the extrudate hole, this fluid being a liquid or a gas and containing a sufficient quantity of at least one solvent of fibrogenic polymer to prevent the said fluid from rapidly coagulating the solution containing the fibrogenic polymer, and the filament made up of this solution surrounding the said fluid is passed through a coagulating bath containing at least one non-solvent of the fibrogenic polymer chosen to rapidly precipitate the external surface of the filament.

9. Procedure according to claim 8, characterized in that the macromolecule with mass greater than 500 comes from the following families: polyvinylpyrrolidone, polyvinylpyridine, polyethylene glycol, polyacrylamide, polyacrylic acids, polyvinyl alcohols.

10. Procedure according to claim 8, characterized in that the surfactant is chosen from among those in which the hydrophobic unit contains a polyoxyethylene chain formation.

11. Procedure according to any one of claims 8 to 10, characterized in that the fluid injected through the hole of the extrudate is made up of the solvent used to dissolve the fibrogenic polymer.

12. Procedure according to any one of claims 8 to 11, characterized in that the additive added to the fibrogenic polymer solution is soluble in the coagulation bath.

13. Application for hollow fibers according to any one of claims 8 to 12 in the area of membrane separation processes.

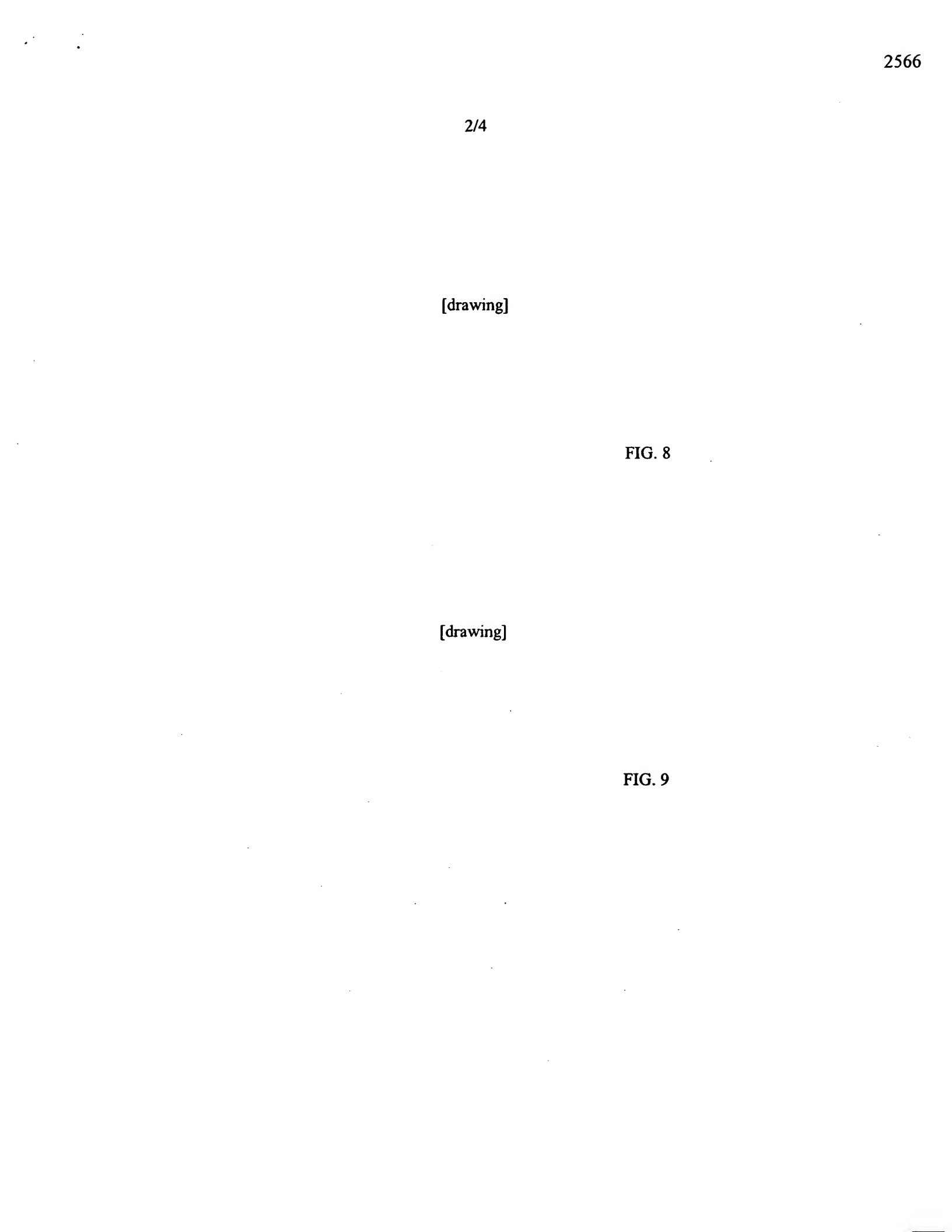


FIG. 8




FIG. 9

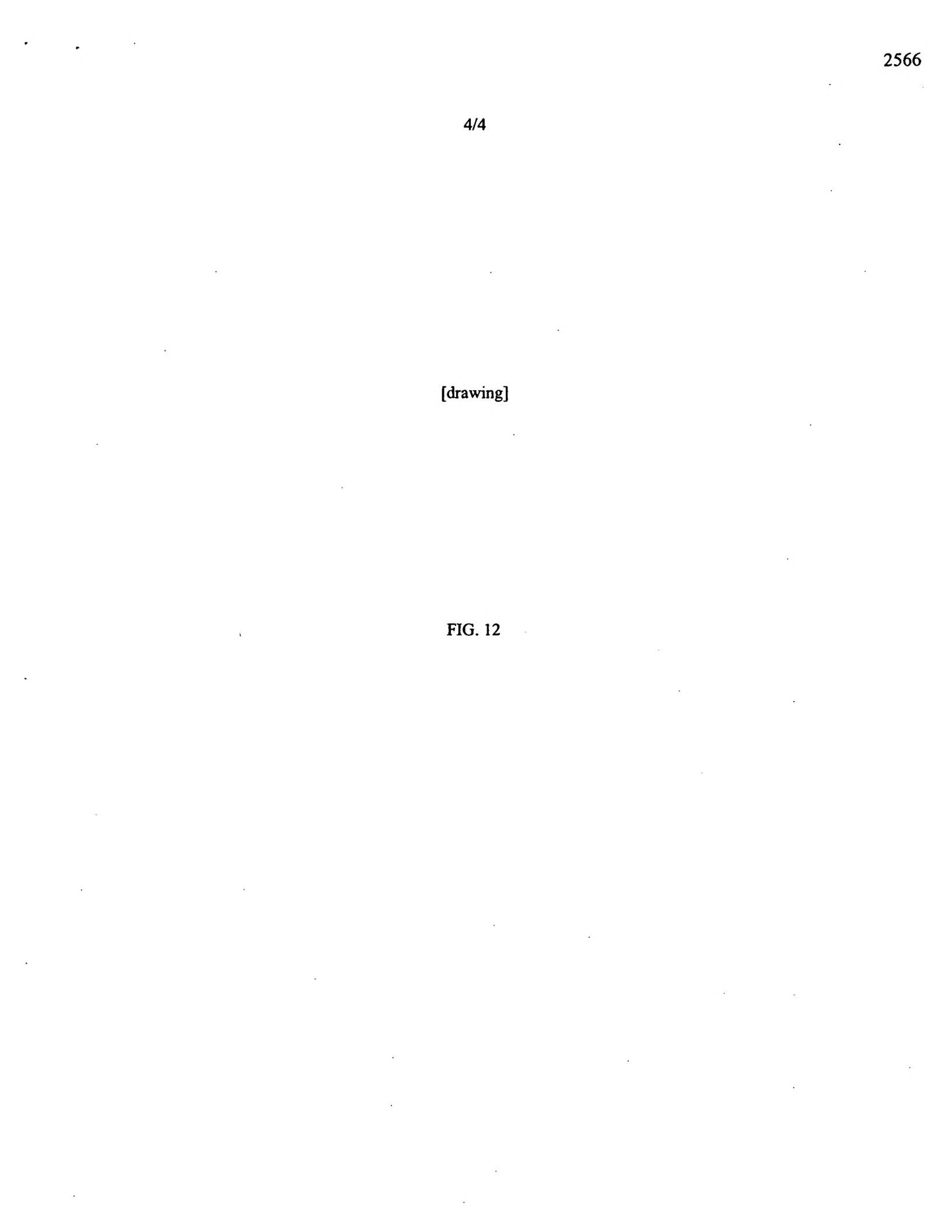


FIG. 12

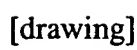

FIG. 1

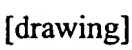

FIG. 2

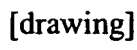

FIG. 3

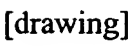

FIG. 4

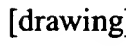

FIG. 5

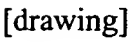

FIG. 6

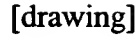

FIG. 7

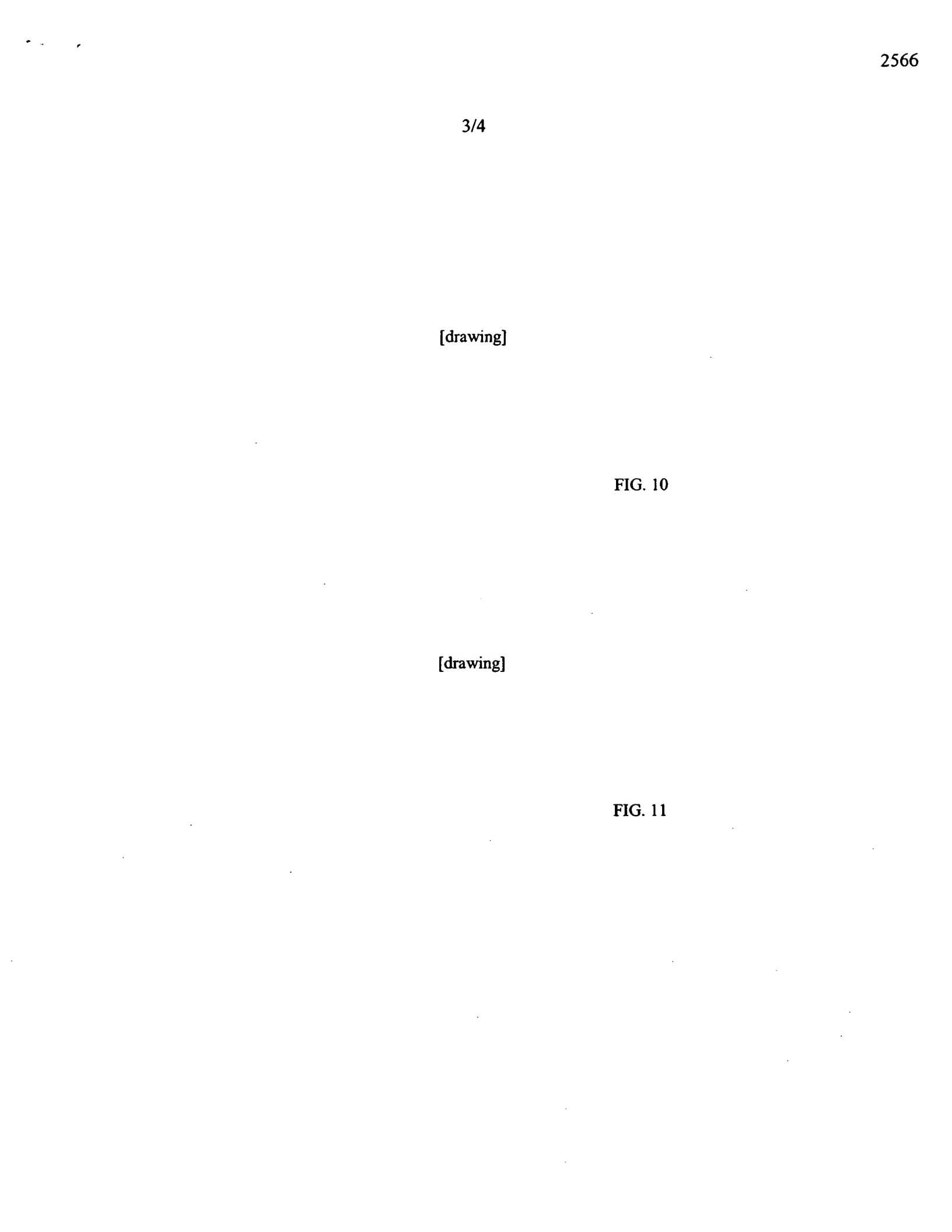

FIG. 10



FIG. 11